

TITLE OF THE INVENTION

Room Temperature Fast-Curable Saturated Hydrocarbon Polymer
Composition and Double-Glazed Glass Pane

5

BACKGROUND OF THE INVENTION

Technical Field

This invention relates to room temperature
10 fast-curable compositions comprising saturated hydrocarbon
polymers as a base polymer, and more particularly, to room
temperature fast-curable compositions of the condensation
cure type having improved fast-cure and deep-cure
capabilities and good water resistance, and double-glazed
15 glass panes using the compositions as a sealant.

Background Art

Elastomeric sealing materials are now on widespread
use in buildings, vehicles and the like. Sealing materials
20 are used for the purpose of establishing a water or air-tight
seal between various members by filling joints or gaps
therebetween. It is thus requisite that once applied to
joints, window frames or the like, sealing materials cure
fast and firmly adhere to various substrates of inorganic
25 materials such as glass, ceramics, metals, cement and mortar
and organic materials such as plastics.

For room temperature fast-curable saturated
hydrocarbon polymers, a primer composition and a bonding
method intended to improve their adhesion are proposed in
30 JP-A 11-209701, but no innovative techniques addressing their
cure speed are known. Intending to improve the cure of RTV
organopolysiloxane compositions, the inventors previously
made research works under the background described below.

Room temperature fast-curable organopolysiloxane
35 compositions of the condensation cure type known in the prior
art include one-package compositions in which the amount of a
crosslinker is minimized to increase the rate of crosslinking

by hydrolysis and two-package compositions in which a crosslinker and a curing agent are separately packed. However, the one-package composition is not regarded as fast-curable because a high speed is available only for curing from the surface and a certain period of time is required for deep curing. The two-package composition is relatively good in deep curing, but is cumbersome to handle because the mixing ratio of two parts is not 1:1, and is thus not compliant with an automatic mixer/dispenser. The amounts of crosslinker and curing agent added must be strictly determined or water must be added as a deep curing agent before the composition can be completely cured to depths. On the other hand, organopolysiloxane compositions of the addition cure type are efficient to work because the mixing ratio of two parts is 1:1, but a heating oven is necessary for curing. In addition, the working environment is restricted since the curing catalysts are poisoned in the presence of addition poisons.

The inventors proposed in JP-A 5-279570 a room temperature fast-curable composition that solved the above-discussed problems. This composition comprises a diorganopolysiloxane or polyoxyalkylene polymer capped with a hydrolyzable silyl group at either end of a molecular chain, an organic compound having at least one carbonyl (C=O) group in a molecule and an organic compound having at least one NH₂ group in a molecule, wherein fast-cure and deep-cure capabilities at room temperature are improved by utilizing water formed as by-product by ketimine-forming reaction between C=O and NH₂ groups by way of dehydrating condensation. The inventors also proposed in JP-A 2001-303024 to apply the above technology to a room temperature fast-curable saturated hydrocarbon polymer composition.

Continuing the research, however, the inventors found that despite favorable fast-cure and deep-cure capabilities, these compositions have problems with respect to water resistance, typically adhesion in the presence of water and

electrical properties after water immersion. Thus the application of these compositions is strictly limited.

It was believed that primary amines left in the cured compositions contribute largely to the above-mentioned
5 decline of water resistance. To solve the problem, the inventors attempted to add an α,β -unsaturated carbonyl compound to the composition for converting a primary amine in the cured composition to a secondary amine, thereby improving water resistance. Adhesion in the presence of water is
10 surely improved, but electrical properties after water immersion still remain problematic, imposing a limit on the application of the composition.

SUMMARY OF THE INVENTION

15 An object of the invention is to provide a room temperature fast-curable saturated hydrocarbon polymer composition of the condensation cure type having improved fast-cure and deep-cure capabilities at room temperature and exhibiting improved adhesion in the presence of water and
20 improved electrical properties after water immersion, and a double-glazed glass pane using the composition as a sealant.

The inventors have found that by using (A) a saturated hydrocarbon polymer having at least one hydrolyzable silyl group at an end of a backbone and/or an end of a side chain
25 per molecule and with a number average molecular weight in the range of 500 to 50,000 as a base polymer, (B) a carbonyl compound having at least two carbonyl groups per molecule, including one carbonyl group and another carbonyl group located at the β -position relative to the one carbonyl group,
30 and (C) an organic compound having at least one NH_2 group per molecule, and selecting components (B) and (C) such that the β -carbonyl group in component (B) is reactive with the NH_2 group in component (C), a room temperature curable saturated hydrocarbon polymer composition of the condensation cure type
35 is formulated which has improved fast-cure and deep-cure properties at room temperature and exhibits improved adhesion

in the presence of water and improved electrical properties after water immersion.

Accordingly the present invention provides a room temperature fast-curable saturated hydrocarbon polymer

5 composition comprising

(A) a saturated hydrocarbon polymer having at least one hydrolyzable silyl group at an end of a backbone and/or an end of a side chain per molecule and with a number average molecular weight in the range of 500 to 50,000,

10 (B) a carbonyl compound having at least two carbonyl groups per molecule, including one carbonyl group and another carbonyl group located at the β -position relative to the one carbonyl group, and

(C) an organic compound having at least one NH_2 group
15 per molecule,

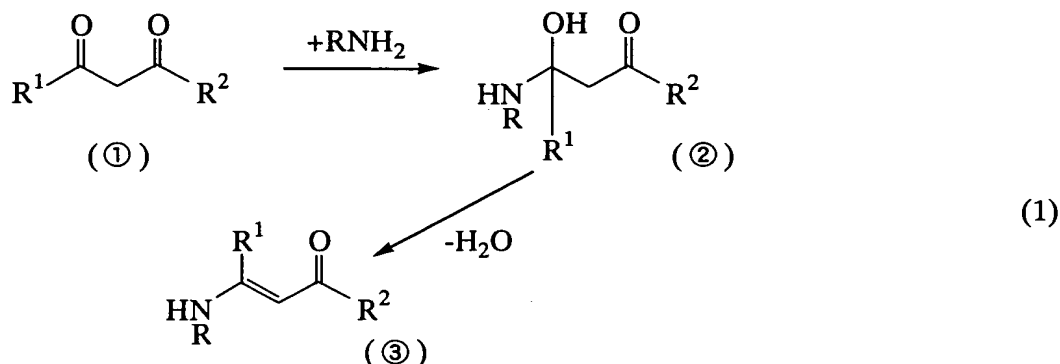
the β -carbonyl group in component (B) being reactive with the NH_2 group in component (C).

Also contemplated herein is a double-glazed glass pane using the composition as a sealant.

20 More particularly, in the composition of the present invention, the β -carbonyl group in component (B) and the NH_2 group in component (C) undergo dehydrating condensation reaction, by way of which water is formed in the deep section of the composition. Consequently, the composition is
25 dramatically improved in fast-cure and deep-cure capabilities. Not relying on the concept that water is intentionally incorporated in the composition as a deep section curing agent, the invention effectively overcomes the problems of water separation and inefficient working due to
30 an increased thixotropy of the composition.

More importantly, the dehydrating condensation reaction of the β -carbonyl group with the NH_2 group is an irreversible reaction as shown by scheme (1). Therefore, the compound having an NH_2 group is never regenerated in the
35 cured composition. Since the composition no longer becomes

more hydrophilic than ever, water resistance and electrical properties after water immersion are dramatically improved.



In the scheme, R and R¹ each are a monovalent organic group, and R² is a monovalent organic group or alkoxy group. The organic group may contain a silicon or oxygen atom. Illustrative of R and R¹ are the same groups as will be exemplified for R³ later. Illustrative examples of R² are R³, alkoxy groups, and those groups to which R³ or silicon-containing organo groups are bonded through an oxygen atom, and preferably alkoxy groups and those groups to which R³ or silicon-containing organo groups are bonded through an oxygen atom.

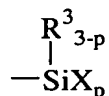
In the above-referred patents JP-A 5-279570 and JP-A 2001-303024, for instance, water is generated by equilibration reaction between a C=O double bond-bearing organic compound and a NH₂ group-bearing organic compound. Thus a ketimine compound exists immediately after curing. Since this reaction is reversible, the ketimine compound gradually decomposes in the presence of moisture to regenerate the NH₂ group-bearing organic compound. The compound thus regenerated makes the cured composition more hydrophilic, allowing easy penetration of water into the cured composition. As a consequence, the cured composition substantially loses water resistance.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Component A

Component (A) is a base polymer. Saturated hydrocarbon polymers (exclusive of polyether polymers) are used. It is
5 requisite that the base polymer be capped with a hydrolyzable silyl group at an end of a backbone and/or an end of a side chain. Owing to the presence of hydrolyzable groups, the polymer undergoes hydrolysis and polycondensation in the presence of water, forming a cured product in the form of a
10 rubbery elastomer.

The hydrolyzable silyl group is in the form of a silicon atom having at least one hydrolyzable group attached thereto and is represented by the following formula.



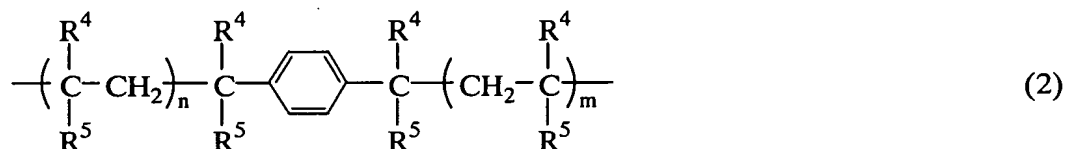
15 Herein, X is a hydrolyzable group, p is an integer of 1 to 3, and R³ is a substituted or unsubstituted monovalent hydrocarbon group.

Examples of the hydrolyzable group represented by X include carboxyl, ketoxime, alkoxy, alkenoxy, amino, aminoxy
20 and amide groups. The number of hydrolyzable groups attached to a silicon atom is not limited to one, and two or three hydrolyzable groups may be attached to a common silicon atom. To the silicon atom to which one or more hydrolyzable groups are attached, other organic groups may, of course, be
25 attached. Examples of such organic groups (R³) include alkyl groups such as methyl, ethyl, and propyl, cycloalkyl groups such as cyclohexyl, alkenyl groups such as vinyl and allyl, aryl groups such as phenyl and tolyl, and substituted forms of the foregoing groups in which some hydrogen atoms are
30 substituted with halogen atoms or the like, such as chloromethyl and 3,3,3-trifluoropropyl.

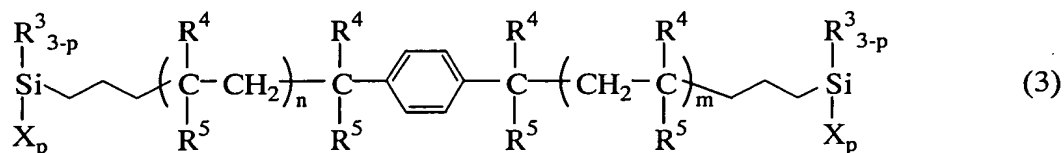
The base polymer (A) should have a number average molecular weight in the range of 500 to 50,000, preferably 700 to 20,000, and more preferably 1,000 to 10,000. Outside

the range, inconvenient issues arise such as difficulty to form a cured rubber having satisfactory properties and inefficient working.

The base polymers are not particularly limited as long as they are saturated hydrocarbon polymers such as ethylene polymers, propylene polymers and isobutylene polymers. Preferred are polymers having in their backbone a structure of the general formula (2):



wherein R^4 and R^5 which may be the same or different are substituted or unsubstituted monovalent hydrocarbon groups, m and n are such positive integers that the polymers have a number average molecular weight in the range of 500 to 50,000. More preferred are polymers having the general formula (3):



wherein R^3 to R^5 which may be the same or different are substituted or unsubstituted monovalent hydrocarbon groups, X is a hydrolyzable group as described above, p is an integer of 1 to 3, m and n are positive integers.

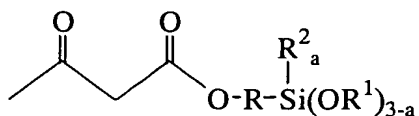
Examples of R^3 to R^5 include the same groups as the organic groups (R^3) other than the hydrolyzable groups exemplified for the hydrolyzable silyl group. The subscripts m and n are such positive integers that the saturated hydrocarbon polymers have a desired number average molecular weight.

Component B

Component (B) is a carbonyl compound having at least two carbonyl groups per molecule, including one carbonyl group and another carbonyl group located at the β -position relative to the one carbonyl group. Such a carbonyl compound is referred to as " β -dicarbonyl compound" and the carbonyl group at the β -position is referred to as " β -carbonyl group," hereinafter. This compound reacts with the NH_2 group-bearing organic compound as component (C) to generate water, which serves as a curing agent, in the deep section of the composition.

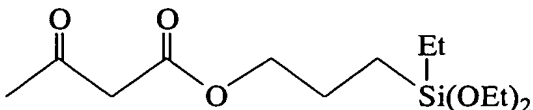
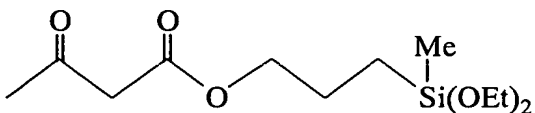
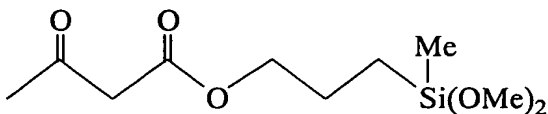
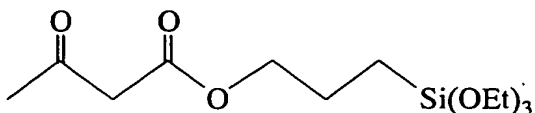
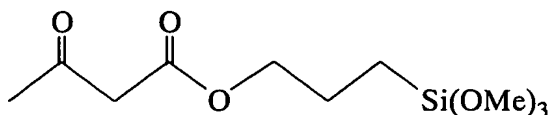
The β -dicarbonyl compound undergoes reaction as shown above by scheme (1). Specifically, it has a molecular structure depicted at circled 1, possessing a moiety in which two carbonyl groups are separated by a carbon atom. Therefore, in order that the β -dicarbonyl compound complete the reaction shown by scheme (1), the carbon atom interposed between two carbonyl groups (i.e., carbon atom at α -position) must not be quaternary, that is, at least one hydrogen atom must be attached to the carbon atom at α -position.

Typical examples of the β -dicarbonyl compound that satisfies the above requirement include, but are not limited to, acetoacetates such as methyl acetoacetate, ethyl acetoacetate, propyl acetoacetate and butyl acetoacetate, diketones such as 2,4-pentanedione, 2,4-hexanedione, and 1,3-cyclohexanedione, and silicon atom-bearing compounds represented by the following formula:



wherein R is a divalent hydrocarbon group, R^1 and R^2 which may be the same or different are substituted or unsubstituted monovalent hydrocarbon groups, and "a" is 0, 1 or 2,

preferably 0 or 1. Illustrative examples of the silicon atom-bearing compounds are shown below.



Herein Me is methyl and Et is ethyl.

5 In addition to the above-mentioned compounds, silane coupling agents, various polymers and oligomers are, of course, useful as long as they contain a moiety having two carbonyl groups separated by a carbon atom as a functional group. These β -dicarbonyl compounds may be used alone or in
10 admixture of two or more. Notably, the β -dicarbonyl compound (B) is preferably a compound having at least one silicon atom.

Component (B) is preferably used in amounts to provide 0.001 to 1 mole, especially 0.01 to 0.1 mole of the
15 β -carbonyl group per 100 g of component (A). Less than 0.001 mole of β -carbonyl group may fail to develop a satisfactory deep cure capability whereas more than 1 mole may produce a cured elastomer having undesirable physical properties.

Component C

Component (C) is an organic compound having at least one NH_2 group per molecule, which is referred to as "amino-bearing organic compound," hereinafter. This compound
5 reacts with the β -dicarbonyl compound as component (B) to generate water serving as a curing agent in the deep section of the composition, as previously described.

Any amino-bearing organic compound may be used as long as it has a reactive primary amino group capable of reaction
10 as shown by scheme (1). Illustrative examples include amines such as methylamine, ethylamine, butylamine, ethylenediamine, and aniline, silane coupling agents having a NH_2 group as a functional group such as γ -aminopropyltriethoxysilane, and polymers and oligomers having NH_2 groups. In the practice of
15 the invention, from the standpoint of steric hindrance during reaction with component (B), it is preferred to use those amino-bearing organic compounds in which the amino group's α -carbon atom is primary or secondary or a member of an aromatic ring. If the α -carbon atom is a tertiary carbon
20 atom as is often the case, its reactivity with a carbonyl group may be low, failing to achieve the desired effect. The amino-bearing organic compounds may be used alone or in admixture of two or more.

Component (C) is preferably used in amounts to provide
25 0.001 to 1 mole, especially 0.01 to 0.1 mole of the primary amino group per 100 g of component (A). Less than 0.001 mole of primary amino group may fail to develop a satisfactory deep cure capability whereas more than 1 mole may produce a cured elastomer having undesirable physical properties.

30

Component D

Component (D) is calcium silicate for imparting resin adhesiveness and appropriate rubber physical properties to the inventive composition. Calcium silicate are preferably
35 in particle form having an average particle diameter of 1 to 50 μm , especially 4 to 40 μm . Calcium silica powder with an

average particle diameter of less than 1 μm may not be filled to fully high levels, resulting in cured rubber with poor physical properties. Calcium silica powder with an average particle diameter of more than 50 μm may make the surface state of the composition rough, detracting from the outer appearance. Preferred calcium silicate has an oil absorption of 10 to 90 ml/100 g, especially 20 to 80 ml/100 g. With an oil absorption of less than 10 ml/100 g, less reinforcement may be achieved, resulting in cured rubber with poor physical properties. An oil absorption of more than 90 ml/100 g may invite a viscosity buildup which interferes with mixing and dispensing upon application. Further preferably, calcium silicate has been surface treated with silane coupling agents and/or siloxanes prior to use.

Component (D) is preferably added in amounts of 5 to 400 parts by weight, more preferably 10 to 300 parts by weight per 100 parts by weight of component (A). Excessive amounts of component (D) may invite a viscosity buildup which interferes with mixing and dispensing upon application. Less amounts of component (D) may degrade the physical properties of cured rubber.

Component E

Component (E) is calcium carbonate which is surface treated with a fatty acid ester. It imparts storage stability, adhesion and appropriate rubber physical properties to the inventive composition. Suitable calcium carbonate to be surface treated may be either heavy calcium carbonate or colloidal calcium carbonate, with the colloidal calcium carbonate being preferred. The fatty acid esters used as the surface treating agent include polyhydric alcohol fatty acid esters such as glycerin fatty acid esters, alpha-sulfo fatty acid esters, polyoxyethylene sorbitan fatty acid esters, sorbitan fatty acid esters, polyethylene fatty acid esters, and sucrose fatty acid esters. The fatty acid esters used herein may be of either low or high molecular weight.

The surface treated state of calcium carbonate and the amount of fatty acid ester borne need not be particularly limited. It is preferred that a minimum sufficient amount of fatty acid ester to provide storage stability be firmly fixed
5 to surfaces of calcium carbonate particles without being liberated by temperature changes. With respect to the manner of surface treatment, calcium carbonate which has already been surface treated with a fatty acid ester may be used. Alternatively, in the process of preparing the inventive
10 composition, a fatty acid ester may be added along with calcium carbonate whereupon calcium carbonate surfaces are treated with the fatty acid ester during the process.

Component (E) is preferably added in amounts of 5 to 400 parts by weight, more preferably 10 to 300 parts by
15 weight per 100 parts by weight of component (A). Excessive amounts of component (E) may invite a viscosity buildup which interferes with mixing and dispensing upon application. Less amounts of component (E) may degrade the physical properties of cured rubber.

20

Component F

Component (F) is a compound obtained by combining 1 mole of γ -aminopropyltrimethoxysilane or
 γ -aminopropyltriethoxysilane with 1.0 to 4.0 moles of
25 γ -glycidoxypropyltrimethoxysilane or γ -glycidoxypropyltriethoxysilane, and heating the mixture at 50°C for 3 days for ripening. It imparts adhesion, especially under water immersion, to the inventive composition. With respect to adhesion, various silane coupling agents were investigated.
30 It was found that silane coupling agents having a primary and/or secondary amino group were effective in imparting initial adhesion, but silane coupling agents having a primary amino group adversely affected adhesion under water immersion. Then, for quenching primary amino groups, we attempted to
35 premix a silane coupling agent having an acrylic, methacrylic or epoxy group with a silane coupling agent having a primary

amino group, and heat the mixture at 50°C for 3 days for ripening. We have found that an effective compound is obtained when the two reactants are mixed in a molar ratio within the above-described range. If the amount of

5 γ -glycidoxypropyltrimethoxysilane or
 γ -glycidoxypropyltriethoxysilane is less than 1.0 mole, some primary amino groups are left behind and may adversely affect adhesion under water immersion. If the said amount is more than 4.0 moles, initial adhesion may become poor. The
10 compounds as component (F) may be used alone or in admixture of two or more.

Component (F) is preferably added in amounts of 0.05 to 30 parts by weight, more preferably 0.1 to 20 parts by weight per 100 parts by weight of component (A). Less
15 amounts of component (F) may fail to develop initial adhesion. Excessive amounts of component (F) may degrade the physical properties of cured rubber.

In the inventive composition, various other compounding ingredients may be incorporated as long as they
20 do not inhibit the fast-cure and deep-cure capabilities at room temperature. Suitable ingredients include condensation catalysts such as organic tin esters, organic tin chelate complexes, organic titanate esters, organic titanium chelate complexes, tetramethylguanidylpropyltrimethoxysilane, and
25 tetramethylguanidylpropyltristrimethylsiloxysilane; storage stabilizers such as methyltrimethoxysilane, vinyltrimethoxysilane, tetramethoxysilane, methyltripropenoxysilane, vinyltripropenoxysilane, phenyltripropenoxysilane, methyltributanoximesilane,
30 vinyltributanoximesilane, tetrabutanoximesilane, and methyltriacetoxysilane; reinforcing fillers such as fumed silica, precipitated silica, titanium dioxide, aluminum oxide, quartz flour, carbon powder, talc and bentonite; basic
35 fillers such as calcium carbonate, zinc carbonate, zinc oxide, and magnesium carbonate; fibrous fillers such as asbestos, glass fibers, carbon fibers and organic fibers; colorants such as pigments and dyes; heat resistance

improvers such as red iron oxide and cerium oxide; freeze resistance improvers; antirusting agents; adhesion improvers such as γ -glycidoxypropyltriethoxysilane; and liquid reinforcements such as network polysiloxane consisting of triorganosiloxy units and SiO_2 units. Any of these ingredients may be added in customary amounts, if necessary.

Additionally, organic solvents, mildew-proof agents, flame retardants, plasticizers, thixotropic agents, tackifiers, cure accelerators, pigments and the like may be added insofar as the objects of the invention are not compromised. Suitable plasticizers include hydrocarbon compounds such as polybutene, hydrogenated polybutene, liquid polybutadiene, hydrogenated polybutadiene, paraffin oil, and naphthenic oil, chlorinated paraffins, phthalates such as dibutyl phthalate and di(2-ethylhexyl) phthalate, non-aromatic dibasic acid esters such as dioctyl adipate and dioctyl sebacate, esters of polyalkylene glycols, and phosphoric acid esters such as tricresyl phosphate.

Curable composition

The inventive composition is generally formulated as a one-package room temperature fast-curable composition by intimately mixing amounts of the above-mentioned components (A) to (F) and optional compounding ingredients in a dry atmosphere. To insure storage stability, the one-package room temperature fast-curable composition may have a microcapsulated form of component (B) or (C) compounded therein, or the components may be formulated as a two-package composition wherein two parts are mixed together prior to use. The two-package composition permits two parts to be mixed at 1:1.

Components (B) and (C) are important for the inventive composition because they react with each other as shown by scheme (1) to produce water serving as a deep curing agent. In the practice of the invention, components (B) and (C) are, of course, selected such that such reaction may quickly take place. Various compounding ingredients which are optionally

used should also be selected so as not to inhibit the production of water.

The inventive composition cures in the presence of airborne moisture and at the same time, water is produced in the deep section. Then not only surface cure, but also deep cure take place. Therefore, both fast-cure and deep-cure capabilities are dramatically improved. In the embodiment of a two-package composition wherein two parts are mixed on use, the invention ensures that the components are divided into two parts to be mixed at 1:1. A further advantage is the ease of practical implementation because both components (B) and (C) are readily available.

Due to fast-cure and deep-cure capabilities, the inventive composition is suited as automotive oil sealing materials and sealing and potting materials for electric and electronic parts which must meet a recent demand for further simplification of process.

The inventive composition can find other applications because of low gas permeability, water resistance and moisture resistance. The composition is highly suited in applications as coating materials requiring water resistance such as ship bottom paint, power plant sea water inlet pipe paint, and fishnet paint, moisture-proof coating materials requiring moisture resistance as used for LCD and PDP, adhesive seals between conductor and resin coating, adhesive seals between a resin case or connector and conductor, adhesive seals in vacuum or pressure chambers, and the like.

In building applications where air-tightness, moisture resistance and/or water resistance is necessary, the invention composition can be advantageously used as adhesive seals between rubber gasket and glass, joint seals for double-glazed glass panes, adhesive seals between juncture sides or edges of water-proof sheet, adhesive seals between solar water panel and roofing water-proof sheet, adhesive seals between solar cell panel and roofing, surface adhesives between siding panel and building wall, and the like. It is also applicable as adhesive seals between glass plates or

transparent resin plates and window frames in meters, instruments or the like.

In particular, the inventive composition is best suited as a sealant for double-glazed glass panes.

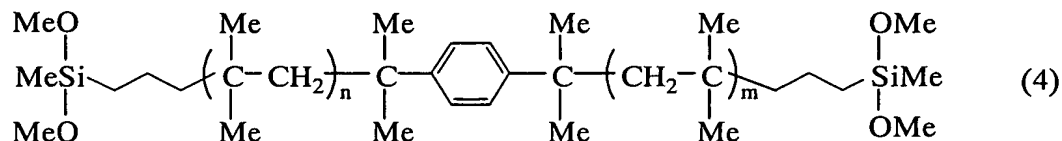
- 5 Double-glazed glass panes using the inventive composition as a sealant are improved in heat insulation efficiency.

EXAMPLE

- 10 Examples of the invention are given below by way of illustration, but not by way of limitation. In the Examples, the viscosity is a measurement at 23°C. Me denotes methyl, Mn is a number average molecular weight, Mw is a weight average molecular weight, and Mw/Mn is a dispersity.

15 Comparative Example 1

- A curable composition was prepared by mixing 150 g of a mixture of a saturated hydrocarbon polymer of the formula (4) below (Mn = 5,800, Mw/Mn = 1.21) and a paraffinic process oil (trade name Diana Process Oil PS-32 by Idemitsu Kosan Co., Ltd.) as hydrocarbon plasticizer in a weight ratio of 2:1, 3.0 g of dibutyltin dilaurate, 75 g of fatty acid-treated light calcium carbonate (trade name Calnex 300 by Maruo Calcium Co. Ltd.), 75 g of heavy calcium carbonate (trade name Softon 1500 by Shiraishi Calcium K.K.), and 10 g of fumed silica (trade name Aerosil R-972 by Nippon Aerosil Co., Ltd.) in a dry state.



(The subscripts m and n are such numbers as to provide Mn = 5,800.)

- 30 The composition was formed into a sheet of 2 mm thick, which was allowed to stand in a 23°C/50% RH atmosphere for one hour. It did not become a rubber elastomer and rubber physical properties could not be examined. Separately, the

composition was poured into a glass cylinder having a diameter of 20 mm and a height of 100 mm and allowed to cure in a 23°C/50% RH atmosphere for 24 hours. At the end of curing, the glass cylinder was broken to take out the cured composition. The portion that became a rubbery elastomer was measured to have a thickness of 0.5 mm.

Comparative Example 2

A curable composition was prepared by mixing 150 g of a mixture of a saturated hydrocarbon polymer of the formula (4) ($M_n = 5,800$, $M_w/M_n = 1.21$) and a paraffinic process oil (trade name Diana Process Oil PS-32 by Idemitsu Kosan Co., Ltd.) as hydrocarbon plasticizer in a weight ratio of 2:1, 75 g of fatty acid-treated light calcium carbonate (trade name Calnex 300 by Maruo Calcium Co. Ltd.), 75 g of heavy calcium carbonate (trade name Softon 1500 by Shiraishi Calcium K.K.), 10 g of fumed silica (trade name Aerosil R-972 by Nippon Aerosil Co., Ltd.), 2.90 g (0.05 mole) of acetone, 6.45 g (0.05 mole) of n-butylamine, and 3.0 g of dibutyltin dilaurate in a dry state.

The composition was formed into a sheet of 2 mm thick, which was allowed to stand in a 23°C/50% RH atmosphere for one hour, obtaining a rubber elastomer. Rubber physical properties were examined according to JIS K-6249, with the results shown in Table 1. A rubber elastomer as cured for 24 hours under the above-mentioned conditions was immersed in water at 50°C for 7 days, after which rubber physical properties were examined according to JIS K-6249. The results are also shown in Table 1. Separately, the composition was cured in a glass cylinder as in Comparative Example 1. The portion that became a rubbery elastomer was measured to have a thickness of 100 mm.

Comparative Example 3

A curable composition was prepared by mixing 150 g of a mixture of a saturated hydrocarbon polymer of the formula (4) ($M_n = 5,800$, $M_w/M_n = 1.21$) and a paraffinic process oil

(trade name Diana Process Oil PS-32 by Idemitsu Kosan Co., Ltd.) as hydrocarbon plasticizer in a weight ratio of 2:1, 75 g of fatty acid-treated light calcium carbonate (trade name Calnex 300 by Maruo Calcium Co. Ltd.), 75 g of heavy calcium carbonate (trade name Softon 1500 by Shiraishi Calcium K.K.), 10 g of fumed silica (trade name Aerosil R-972 by Nippon Aerosil Co., Ltd.), 7.35 g (0.05 mole) of cyclohexanone, 7.45 g (0.05 mole) of cyclohexylamine, and 3.0 g of dibutyltin dilaurate in a dry state.

As in Comparative Example 2, the composition was cured into a rubber elastomer, and its physical properties were examined. The results are shown in Table 1. Separately, the composition was cured in a glass cylinder as in Comparative Example 1. The portion that became a rubbery elastomer was measured to have a thickness of 100 mm.

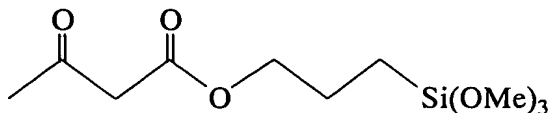
Example 1

A curable composition was prepared by mixing 150 g of a mixture of a saturated hydrocarbon polymer of the formula (4) ($M_n = 5,800$, $M_w/M_n = 1.21$) and a paraffinic process oil (trade name Diana Process Oil PS-32 by Idemitsu Kosan Co., Ltd.) as hydrocarbon plasticizer in a weight ratio of 2:1, 75 g of fatty acid-treated light calcium carbonate (trade name Calnex 300 by Maruo Calcium Co. Ltd.), 75 g of heavy calcium carbonate (trade name Softon 1500 by Shiraishi Calcium K.K.), 10 g of fumed silica (trade name Aerosil R-972 by Nippon Aerosil Co., Ltd.), 6.5 g (0.05 mole) of ethyl acetoacetate, 9.0 g (0.05 mole) of γ -aminopropyltrimethoxysilane, and 3.0 g of dibutyltin dilaurate in a dry state.

As in Comparative Example 2, the composition was cured into a rubber elastomer, and its physical properties were examined. The results are shown in Table 1. Separately, the composition was cured in a glass cylinder as in Comparative Example 1. The portion that became a rubbery elastomer was measured to have a thickness of 100 mm.

Example 2

A curable composition was prepared as in Example 1 except that 13.2 g (0.05 mole) of a compound shown below was used instead of 6.5 g of ethyl acetoacetate.

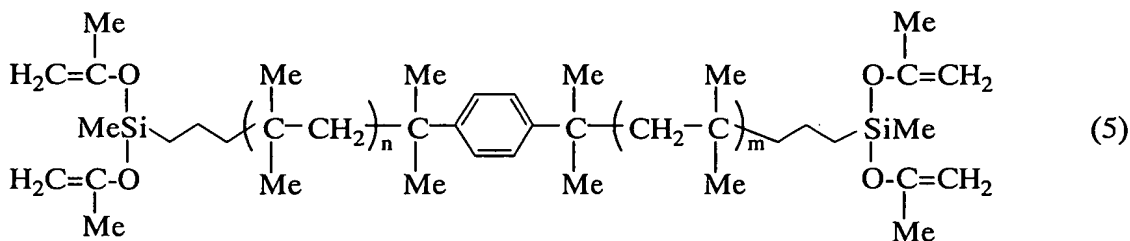


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As in Comparative Example 2, the composition was cured into a rubber elastomer, and its physical properties were examined. The results are shown in Table 1. Separately, the composition was cured in a glass cylinder as in Comparative
10 Example 1. The portion that became a rubbery elastomer was measured to have a thickness of 100 mm.

Comparative Example 4

A curable composition was prepared by mixing 150 g of
15 a mixture of a saturated hydrocarbon polymer of the formula (5) below ($M_n = 5,800$, $M_w/M_n = 1.21$) and a paraffinic process oil (trade name Diana Process Oil PS-32 by Idemitsu Kosan Co., Ltd.) as hydrocarbon plasticizer in a weight ratio of 2:1, 1.0 g of tetramethylguanidylpropyltrimethoxysilane, 75 g
20 of fatty acid-treated light calcium carbonate (trade name Calnex 300 by Maruo Calcium Co. Ltd.), 75 g of heavy calcium carbonate (trade name Softon 1500 by Shiraishi Calcium K.K.), and 10 g of fumed silica (trade name Aerosil R-972 by Nippon Aerosil Co., Ltd.) in a dry state.



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(The subscripts m and n are such numbers as to provide $M_n = 5,800$.)

The composition was formed into a sheet of 2 mm thick, which was allowed to stand in a 23°C/50% RH atmosphere for one hour. It did not become a rubber elastomer and rubber physical properties could not be examined. Separately, the composition was poured into a glass cylinder having a diameter of 20 mm and a height of 100 mm and allowed to cure in a 23°C/50% RH atmosphere for 24 hours. At the end of curing, the glass cylinder was broken to take out the cured composition. The portion that became a rubbery elastomer was measured to have a thickness of 0.6 mm.

Comparative Example 5

A curable silicone rubber composition was prepared by mixing 150 g of a mixture of a saturated hydrocarbon polymer of the formula (5) ($M_n = 5,800$, $M_w/M_n = 1.21$) and a paraffinic process oil (trade name Diana Process Oil PS-32 by Idemitsu Kosan Co., Ltd.) as hydrocarbon plasticizer in a weight ratio of 2:1, 2.90 g (0.05 mole) of acetone, 6.45 g (0.05 mole) of n-butylamine, 1.0 g of tetramethylguanidylpropyltrimethoxysilane, 75 g of fatty acid-treated light calcium carbonate (trade name Calnex 300 by Maruo Calcium Co. Ltd.), 75 g of heavy calcium carbonate (trade name Softon 1500 by Shiraishi Calcium K.K.), and 10 g of fumed silica (trade name Aerosil R-972 by Nippon Aerosil Co., Ltd.) in a dry state.

As in Comparative Example 2, the composition was cured into a rubber elastomer, and its physical properties were examined. The results are shown in Table 2. Separately, the composition was cured in a glass cylinder as in Comparative Example 1. The portion that became a rubbery elastomer was measured to have a thickness of 100 mm.

Comparative Example 6

A curable silicone rubber composition was prepared by mixing 150 g of a mixture of a saturated hydrocarbon polymer of the formula (5) ($M_n = 5,800$, $M_w/M_n = 1.21$) and a paraffinic process oil (trade name Diana Process Oil PS-32 by

Idemitsu Kosan Co., Ltd.) as hydrocarbon plasticizer in a weight ratio of 2:1, 7.35 g (0.05 mole) of cyclohexanone, 7.45 g (0.05 mole) of cyclohexylamine, 1.0 g of tetramethylguanidylpropyltrimethoxysilane, 75 g of fatty acid-treated light calcium carbonate (trade name Calnex 300 by Maruo Calcium Co. Ltd.), 75 g of heavy calcium carbonate (trade name Softon 1500 by Shiraishi Calcium K.K.), and 10 g of fumed silica (trade name Aerosil R-972 by Nippon Aerosil Co., Ltd.) in a dry state.

As in Comparative Example 2, the composition was cured into a rubber elastomer, and its physical properties were examined. The results are shown in Table 2. Separately, the composition was cured in a glass cylinder as in Comparative Example 1. The portion that became a rubbery elastomer was measured to have a thickness of 100 mm.

Example 3

A curable silicone rubber composition was prepared by mixing 150 g of a mixture of a saturated hydrocarbon polymer of the formula (5) ($M_n = 5,800$, $M_w/M_n = 1.21$) and a paraffinic process oil (trade name Diana Process Oil PS-32 by Idemitsu Kosan Co., Ltd.) as hydrocarbon plasticizer in a weight ratio of 2:1, 7.9 g (0.05 mole) of butyl acetoacetate, 11.05 g (0.05 mole) of γ -aminopropyltriethoxysilane, 1.0 g of tetramethylguanidylpropyltrimethoxysilane, 75 g of fatty acid-treated light calcium carbonate (trade name Calnex 300 by Maruo Calcium Co. Ltd.), 75 g of heavy calcium carbonate (trade name Softon 1500 by Shiraishi Calcium K.K.), and 10 g of fumed silica (trade name Aerosil R-972 by Nippon Aerosil Co., Ltd.) in a dry state.

As in Comparative Example 2, the composition was cured into a rubber elastomer, and its physical properties were examined. The results are shown in Table 2. Separately, the composition was cured in a glass cylinder as in Comparative Example 1. The portion that became a rubbery elastomer was measured to have a thickness of 100 mm.

Table 1

		Comparative Example			Example	
		1	2	3	1	2
Initial	Hardness, Durometer A	UM	16	17	20	23
	Elongation at break, %	UM	550	520	600	580
	Tensile strength, MPa	UM	0.95	1.05	1.40	1.50
After water immersion	Hardness, Durometer A	-	4	6	19	23
	Elongation at break, %	-	200	220	610	590
	Tensile strength, MPa	-	0.15	0.23	1.35	1.48

UM: unmeasurable

5

Table 2

		Comparative Example			Example
		4	5	6	3
Initial	Hardness, Durometer A	UM	18	20	24
	Elongation at break, %	UM	500	510	450
	Tensile strength, MPa	UM	1.01	1.02	1.80
After water immersion	Hardness, Durometer A	-	6	8	24
	Elongation at break, %	-	170	180	500
	Tensile strength, MPa	-	0.18	0.26	1.77

UM: unmeasurable

Each of the curable compositions prepared in Examples 1 and 3 and Comparative Examples 3 and 6 was formed into a sheet of 1 mm thick, which was allowed to stand in a 23°C/50% RH atmosphere for 24 hours. The cured sheet was measured for electrical properties at the initial and after 24 hour immersion in water at 20°C according to JIS C-2123. The results are shown in Table 3.

Table 3

	Volume resistivity ($\Omega \cdot \text{cm}$)	
Example 1	Initial	4.0×10^{11}
	After water immersion	3.5×10^{10}
Example 3	Initial	2.0×10^{11}
	After water immersion	1.0×10^{10}
Comparative Example 3	Initial	2.0×10^{11}
	After water immersion	Unmeasurable
Comparative Example 6	Initial	1.0×10^{11}
	After water immersion	Unmeasurable

It is seen from the data of Table 3 that the cured sheets obtained from the inventive compositions (Examples 1 and 3) have electrical properties which are kept stable (or little changed from the initial) even after water immersion.

Comparative Example 7

A curable composition was prepared by mixing 150 g of a mixture of a saturated hydrocarbon polymer of the formula (4) ($M_n = 5,800$, $M_w/M_n = 1.21$) and a paraffinic process oil (trade name Diana Process Oil PS-32 by Idemitsu Kosan Co., Ltd.) as hydrocarbon plasticizer in a weight ratio of 2:1, 75 g of fatty acid-treated light calcium carbonate (trade name Calnex 300 by Maruo Calcium Co. Ltd.), 75 g of heavy calcium carbonate (trade name Softon 1500 by Shiraishi Calcium K.K.), 10 g of fumed silica (trade name Aerosil R-972 by Nippon Aerosil Co., Ltd.), 7.35 g (0.05 mole) of cyclohexanone, 7.45 g (0.05 mole) of cyclohexylamine, 3.0 g of dibutyltin dilaurate and 18.0 g (0.1 mole) of γ -aminopropyltrimethoxysilane in a dry state.

As in Comparative Example 2, the composition was cured into a rubber elastomer, and its physical properties were examined. The results are shown in Table 4. Separately, the

composition was cured in a glass cylinder as in Comparative Example 1. The portion that became a rubbery elastomer was measured to have a thickness of 100 mm.

5 Example 4

 A curable composition was prepared by mixing 150 g of a mixture of a saturated hydrocarbon polymer of the formula (4) ($M_n = 5,800$, $M_w/M_n = 1.21$) and a paraffinic process oil (trade name Diana Process Oil PS-32 by Idemitsu Kosan Co., Ltd.) as hydrocarbon plasticizer in a weight ratio of 2:1, 150 g of calcium silicate (NYAD G by NYCO'S VERSATILE MINERAL, average particle diameter 40 μm , oil absorption 45 ml/100 g), 6.5 g (0.05 mole) of ethyl acetoacetate, 9.0 g (0.05 mole) of γ -aminopropyltrimethoxysilane, and 3.0 g of dibutyltin dilaurate in a dry state.

 As in Comparative Example 2, the composition was cured into a rubber elastomer, and its physical properties were examined. The results are shown in Table 4. Separately, the composition was cured in a glass cylinder as in Comparative Example 1. The portion that became a rubbery elastomer was measured to have a thickness of 100 mm.

Example 5

 A curable composition was prepared by mixing 150 g of a mixture of a saturated hydrocarbon polymer of the formula (4) ($M_n = 5,800$, $M_w/M_n = 1.21$) and a paraffinic process oil (trade name Diana Process Oil PS-32 by Idemitsu Kosan Co., Ltd.) as hydrocarbon plasticizer in a weight ratio of 2:1, 150 g of fatty acid ester-treated light calcium carbonate (trade name Sealets 500 by Maruo Calcium Co., Ltd.), 6.5 g (0.05 mole) of ethyl acetoacetate, 9.0 g (0.05 mole) of γ -aminopropyltrimethoxysilane, and 3.0 g of dibutyltin dilaurate in a dry state.

 As in Comparative Example 2, the composition was cured into a rubber elastomer, and its physical properties were examined. The results are shown in Table 4. Separately, the

composition was cured in a glass cylinder as in Comparative Example 1. The portion that became a rubbery elastomer was measured to have a thickness of 100 mm. It is seen that the inventive composition is improved in deep cure.

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Example 6

A curable composition was prepared by mixing, in a dry state, 150 g of a mixture of a saturated hydrocarbon polymer of the formula (4) ($M_n = 5,800$, $M_w/M_n = 1.21$) and a
10 paraffinic process oil (trade name Diana Process Oil PS-32 by Idemitsu Kosan Co., Ltd.) as hydrocarbon plasticizer in a weight ratio of 2:1, 150 g of calcium silicate (NYAD G by NYCO'S VERSATILE MINERAL, average particle diameter 40 μm , oil absorption 45 ml/100 g), 6.5 g (0.05 mole) of ethyl
15 acetoacetate, 9.0 g (0.05 mole) of γ -aminopropyltrimethoxysilane, 3.0 g of dibutyltin dilaurate, and 18 g of the compound obtained by heating 1 mole of γ -aminopropyltrimethoxysilane and 2 moles of γ -glycidoxypentyltrimethoxysilane at 50°C for 3 days for ripening.

20 As in Comparative Example 2, the composition was cured into a rubber elastomer, and its physical properties were examined. The results are shown in Table 4. Separately, the composition was cured in a glass cylinder as in Comparative Example 1. The portion that became a rubbery elastomer was
25 measured to have a thickness of 100 mm. It is seen that the inventive composition is improved in deep cure.

Each of the curable compositions prepared in Examples 4 to 6 and Comparative Example 7 was cast on float glass to form a simple adhesion test specimen, which was cured in an
30 atmosphere of $23 \pm 2^\circ C$ and $50 \pm 5\%$ RH for 7 days. Initial adhesion (percent cohesive failure) was measured at this point. The specimen was immersed in a thermostat water tank at 55°C for 50 days, after which adhesion after water immersion was examined.

Table 4

		Comparative Example	Example			
		7	4	5	6	
Initial	Hardness, Durometer A	18	25	22	25	
	Elongation at break, %	550	550	620	560	
	Tensile strength, MPa	1.10	2.00	1.80	2.05	
After water immersion	Hardness, Durometer A	4	24	23	25	
	Elongation at break, %	200	560	680	550	
	Tensile strength, MPa	0.21	1.90	1.75	2.00	
Initial	Simple adhesion, CF%	80	90	90	100	
After water immersion	Simple adhesion, CF%	0	80	70	100	

Comparative Example 8

5 A curable composition was prepared by mixing 150 g of
a trimethoxysilyl end-capped dimethyl polymer having a
viscosity of 20,000 centipoise at 25°C, 75 g of colloidal
light calcium carbonate (trade name MT-100 by Maruo Calcium
Co., Ltd.), 75 g of heavy calcium carbonate (trade name
10 Softon 1500 by Shiraishi Calcium K.K.), 10 g of fumed silica
(trade name Aerosil R-972 by Nippon Aerosil Co., Ltd.), 6.5 g
(0.05 mole) of ethyl acetoacetate, 9.0 g (0.05 mole) of
 γ -aminopropyltrimethoxysilane, and 3.0 g of dibutyltin
dilaurate in a dry state.

15 Each of the curable compositions prepared in Examples
1 and 3 and Comparative Example 8 was formed into a sheet of
2 mm thick, which was allowed to stand in a 23°C/50% RH
atmosphere for 24 hours. The cured sheet of 2 mm thick was
measured for water vapor permeability according to JIS
20 Z-0208, using a full automatic water vapor permeability
tester L80-4000H model. The results are shown in Table 5.

Table 5

	Water vapor permeability (g/m ² ·day)
Example 1	1
Example 3	1
Comparative Example 8	40

It is seen from the data of Table 5 that the cured
5 products of the inventive compositions (Examples 1 and 3) are
least permeable to water vapor and exhibit better sealing
performance.

It is evident that the room temperature curable
composition of the condensation cure type comprising a
10 saturated hydrocarbon polymer as a base polymer according to
the invention is dramatically improved in fast-cure and
deep-cure capabilities without sacrificing adhesion and
electrical properties after water immersion.

Japanese Patent Application No. 2003-105637 is
15 incorporated herein by reference.

Although some preferred embodiments have been
described, many modifications and variations may be made
thereto in light of the above teachings. It is therefore to
be understood that the invention may be practiced otherwise
20 than as specifically described without departing from the
scope of the appended claims.